

WHAT IS CLAIMED IS:

1. A process for the enhancement of a used metal catalyst for the catalytic hydrogenation of carbon monoxide, said catalyst comprising one or  
5 more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re and Pt, the process comprising:
  - a) decreasing the hydrocarbon content thereof;
  - b) calcining under an oxidant-containing atmosphere;
  - c) impregnating with a solution of a compound of at least one metal  
10 selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re, Pt, Mo, W, Si, Cr, Ti, Mg, Mn, Zr, Hf, Al, Th, La, Ce and Y;
  - d) calcining under an oxidant-containing atmosphere; and
  - e) reducing with a hydrogen-containing gas at elevated temperatures thereby forming an active catalyst.
- 15 2. A process in accordance with Claim 1, wherein step a) is carried out by one of the following:
  - contacting with a hydrogen-containing gas at elevated temperatures;
  - treating with a solvent or supercritical fluid;
  - 20 treating with a solvent or supercritical fluid and then contacting with a hydrogen-containing gas at elevated temperatures;
  - contacting with an oxygen-containing gas or steam at elevated temperatures and then contacting with a hydrogen-containing gas at elevated temperatures; and
  - 25 treating with a solvent or supercritical fluid, contacting with an oxygen-containing gas or steam at elevated temperatures and then contacting with a hydrogen-containing gas at elevated temperatures.

3. A process in accordance with Claim 1, wherein the impregnation solution in step c) contains a compound of a metal selected from the group consisting of cobalt, ruthenium, copper and nickel.

5        4. A process in accordance with Claim 1, wherein the metal compound in step c) is a metal salt selected from the group consisting of nitrate, acetate, formate, citrate and carbonate.

10       5. A process in accordance with Claim 1, wherein the impregnation solution in step c) contains a salt of the same metal as the catalyst metal.

15       6. A process in accordance with Claim 1 wherein said oxidant in step b) or d) is selected from the group consisting of oxygen, air, ozone and nitrogen oxides.

15       7. A process in accordance with Claim 1 wherein the amount of said impregnating solution utilized in step c) is from about 10% to 5,000% of the calculated pore volume of the catalyst.

20       8. A process in accordance with Claim 1 additionally including the step of passivating after step e) by:

          treatment with a carbon monoxide-containing gas under conditions such that the carbon monoxide is not significantly decomposed; or

25       treatment with a gas containing carbon monoxide and hydrogen under conditions such that the carbon monoxide is not significantly hydrogenated.

          9. A process in accordance with Claim 1, wherein said catalyst comprises cobalt

10. A process for the catalytic hydrogenation of carbon monoxide to produce a mixture of hydrocarbons in a carbon monoxide hydrogenation reactor utilizing a used catalyst comprising one or more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re and Pt, at least a portion  
5 of the catalyst having been enhanced by a process comprising:

- a) decreasing the hydrocarbon content thereof;
- b) calcining under an oxidant-containing atmosphere;
- c) impregnating with a solution of a compound of at least one metal selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re, Pt, Mo,  
10 W, Si, Cr, Ti, Mg, Mn, Zr, Hf, Al, Th, La, Ce and Y;
- d) calcining under an oxidant-containing atmosphere; and
- e) reducing with a hydrogen-containing gas at elevated temperatures thereby forming an active catalyst.

15 11. A process in accordance with Claim 10, additionally including the step of removing catalyst fines by

- i) classification or screening of a powder obtained in any step producing a powder; or
- ii) decanting or classification of a catalyst slurry in any step producing a  
20 slurry.

12. A process in accordance with Claim 10, wherein said catalyst is a supported catalyst.

25 13. A process in accordance with Claim 10, wherein said catalyst is a Dispersed Active Metal (DAM) catalyst.

14. A process in accordance with Claim 10, wherein said catalyst comprises cobalt.

15. A process according to claim 10 wherein steps (a through (e are carried out in a single carbon monoxide hydrogenation reactor.

5           16. A process according to claim 15 wherein the carbon monoxide hydrogenation reactor is a fixed bed reactor

17. A process according to claim 10, additionally including the steps of withdrawing catalyst from a reactor and returning it to at least one reactor,  
10 wherein steps (a through (e are carried out subsequent to said withdrawing step.

18. A process according to claim 17, where steps (a through (e are carried out prior to said returning step.

15           19. A process according to claim 17, where steps (a through (e are carried out subsequent to said returning step.

20. A process according to claim 10, additionally including the steps of withdrawing catalyst from a reactor and returning it to at least one reactor,  
20 wherein at least one of steps (a through (e is carried out prior to said withdrawing step.

21. A process according to claim 20, wherein at least one of steps (b through (e is carried out prior to said returning step.

25

22. A process according to claim 10, additionally including the steps of withdrawing catalyst from a reactor and returning it to at least one reactor, wherein at least one of steps (a through (d is carried out prior to said

withdrawing step, and at least one of steps (b through (e is carried out subsequent to said returning step.

23. A process according to claim 22 wherein the catalyst is passivated  
5 after step a) and then withdrawn from the reactor

24. A process according to claim 17, wherein said reactors are slurry reactors and the catalyst is withdrawn as a mixture with hydrocarbons.

10 25. A process in accordance with Claim 24, wherein in step a) the catalyst particles are initially separated from the mixture.

26. A process in accordance with Claim 25, wherein the catalyst particles are separated by filtration, or by gravitational or centrifugal separation followed  
15 by decanting the hydrocarbons from the catalyst particles.

27. A process in accordance with Claim 24, wherein the treated catalyst is returned in at least one slurry reactor by one or more of:

forming a slurry of the catalyst with liquid hydrocarbons and introducing  
20 said slurry into said reactor;

forming a suspension of the catalyst in a non-oxidizing gas and introducing said suspension into said reactor; or

transferring the catalyst to the reactor by gravity or pressure gradient.

25 28. A process in accordance with Claim 24, wherein said catalyst is withdrawn periodically during operation of at least one slurry reactor

29. A process according to claim 24, wherein at least a portion of said catalyst is returned to at least one slurry reactor during operation thereof.

30. A process in accordance with Claim 24, wherein said catalyst is withdrawn continuously during operation of at least one slurry reactor

5        31. A catalyst for the hydrogenation of carbon monoxide, comprising one or more members selected from the group consisting of Co, Ni, Cu, Ru, Rh, Pd, Os, Ir, Re and Pt, said catalyst being enhanced by the process of claim 1.

10       32. A process for producing higher hydrocarbons by the hydrogenation of carbon monoxide by reaction with hydrogen at reaction conditions in the presence of an enhanced catalyst according to Claim 31.

15       33. A process in accordance with Claim 32, wherein at least a portion of the hydrocarbons formed are upgraded to more valuable products by at least one of fractionation and conversion operations.